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(54) Title: METHOD OF MODIFYING SOURCE CHEMICALS IN AN ALD PROCESS

(57) Abstract: This invention concerns a method for modifying a source material used in an ALD process, a method for depositing transition metal nitride thin films by an ALD process and apparatus for use in such process. According to the present invention transition metal source materials are reduced by vaporizing a metal source material, conducting the vaporized metal source material, into a reducing zone comprising a solid reducing agent maintained at an elevated temperature. Thereafter, the metal source material is contacted with the solid or liquid reducing agent in order to convert the source material into a reduced metal compound and reaction byproducts having a sufficiently high vapor pressure for transporting in gaseous form.

**METHOD OF MODIFYING SOURCE CHEMICALS IN AN ALD PROCESS****Background of the Invention****5 Field of the Invention**

The present invention relates to metal nitride thin films. In particular, the present invention concerns a method of *in situ* reduction of source chemicals as well as a method of growing of metal nitride thin films. The present invention also relates to an apparatus for growing thin films on a substrate by an ALD type process.

**10 Description of Related Art**

The integration level of components in integrated circuits is increasing, which rapidly brings about a need for a decrease of the size of components and interconnects. Design rules are setting the feature sizes to  $\leq 0.2 \mu\text{m}$ . Deposition of uniform thin films on wafer surfaces by Physical Vapor Deposition (referred to as PVD hereinafter) and Chemical Vapor Deposition (referred to as CVD hereinafter) methods has become difficult due to small feature sizes. As a result, complete film coverage on deep bottoms of vias and trenches cannot be obtained. PVD methods require more or less direct line-of-sight on the surfaces to be coated. Traditional CVD methods require rather precise concentration control of the source chemicals and good temperature uniformity over the substrate. Deep bottoms may have a local "microclimate" where the variable concentration of source chemical vapors is causing non-uniform growth of thin film.

25

Integrated circuits contain interconnects which are usually made of aluminium or copper. Especially copper is prone to diffusion to the surrounding materials. Diffusion affects the electrical properties of the circuits and active components may malfunction. The diffusion of metals from interconnects into the active parts of the devices is prevented with an electrically conductive diffusion barrier layer. Favoured diffusion barriers are, e.g., amorphous transition metal nitrides, such as TiN, TaN and WN. The nitrides can be non-stoichiometric because nitrogen is located at interstitial position of the lattice.

Atomic Layer Deposition (ALD), originally, Atomic Layer Epitaxy (ALE) is an advanced variation of CVD. The method name was changed from ALE into ALD to avoid possible confusion when discussing about polycrystalline and amorphous thin films. The ALD method is based on sequential self-saturated surface reactions. The method is described in 5 detail in US Patents Nos. 4,058,430 and 5,711,811. The reactor benefits from the usage of inert carrier and purging gases which makes the system fast.

The separation of source chemicals from each other by inert gases prevents gas-phase reactions between gaseous reactants and enables self-saturated surface reactions leading to 10 film growth which requires neither strict temperature control of the substrates nor precise dosage control of source chemicals. Surplus chemicals and reaction byproducts are always removed from the reaction chamber before the next reactive chemical pulse is introduced into the chamber. Undesired gaseous molecules are effectively expelled from the reaction chamber by keeping the gas flow speeds high with the help of an inert purging gas. The 15 purging gas pushes the extra molecules towards the vacuum pump used for maintaining a suitable pressure in the reaction chamber. ALD provides an excellent and automatic self-control for the film growth.

In case of transition metal nitrides, reduction of the metal source material is needed in 20 order to increase the amount of metal in the nitride and, thus, to lower the resistivity of the nitride. "Reduction" can be defined as any reaction, wherein the metal of the source chemical receives electrons and its oxidation state decreases.

In the art, it is known to reduce the metal source material by pulsing a reducing agent after 25 the metal source material pulse. A number of different chemicals have been used for the reduction. For example, tungsten compounds have been reduced by using hydrogen ( $H_2$ ) (US 5,342,652 and EP-A2-0 899 779), silanes such as  $SiH_4$  (US 5,691,235) and chlorosilanes such as  $SiHCl_3$  (US 5,723,384). Low oxidation-state metal chlorides can also be synthesized by passing a gaseous mixture of hydrogen chloride (HCl) and hydrogen 30 ( $H_2$ ) over a heated metal (US Patent No. 4,803,127).

Reduction of  $WF_6$  into W metal on substrate surfaces by using a silane,  $Si_2H_6$ , is disclosed by J. W. Klaus (Atomic Layer Deposition of Tungsten and Tungsten Nitride Using Sequential Surface Reactions, AVS 46<sup>th</sup> International Symposium, abstract TF-

TuM6, <http://www.vacuum.org/symposium/seattle/technical.html>, to be presented on the 26<sup>th</sup> of October, 1999 in Seattle, USA).

There are, however, drawbacks related to these prior art methods. Silanes may also react  
5 with WF<sub>6</sub>, thus forming tungsten silicides, such as WSi<sub>2</sub>. Hydrogen can reduce a tungsten compound into tungsten metal which has too low vapor pressure for being transported in gas phase onto substrates.

- Various metal species adsorbed on substrate surfaces have been reduced with zinc in ALE processes (cf., e.g., L. Hiltunen, M. Leskelä, M. Mäkelä, L. Niinistö, E. Nykänen, P. Soininen, "Nitrides of Titanium, Niobium, Tantalum and Molybdenum Grown as Thin Films by the Atomic Layer Epitaxy Method", Thin Solid Films, 166 (1988) 149 – 154). In the known processes, the additional zinc vapor used during the deposition decreased the resistivity of the nitride film either by increasing the metal-to-nitrogen ratio or by removing  
10 oxygen from the films. The known process comprised the following pulsing order: a metal source chemical vapor pulse / an inert gas purge / a zinc vapor pulse / an inert gas purge / a nitrogen source chemical vapor pulse / an inert gas purge. A basic problem related to reduction carried out with the zinc vapor method is that thin films contaminated with zinc metal and its compounds should be avoided in processes used for the manufacture of  
15 integrated circuits (referred to as IC hereinafter). Diffusing zinc can destroy the active components of the IC's. Additionally, the low end of the substrate temperature range is probably limited by the volatility of zinc metal and the sticking coefficient of zinc compounds on the surface.  
20  
25 In addition to zinc, hydrogen and magnesium have also been tested as reducing agents in ALE processes. The results have not been promising. Hydrogen is not capable enough of reducing the metal compounds at low substrate temperatures. Magnesium forms on the substrate surface a halide which has a very low vapor pressure and stops film growth. It seems that the applicability of elemental reduction on the substrate surface is rather limited.  
30 Few elements have high enough vapor pressure to be used as ALD source chemicals. Even fewer gaseous elements form a volatile byproduct during the reduction step.

A method for influencing the properties of CVD source chemicals is disclosed by C.-Y. Lee [The Preparation of Titanium-Based Thin Film by CVD Using Titanium Chlorides as

Precursors, Chem. Vap. Deposition, 5 (1999) 69 – 73)]. According to the publication, in a CVD process  $TiCl_4$  vapor was flowing over titanium metal which was heated to 900 °C. The reaction produced  $TiCl_x$  ( $x < 4$ ) subchlorides. These subchlorides were downstream thermally decomposed into Ti metal on a substrate which was heated to 500 - 800 °C.

5

The CVD reducing apparatus described by C.-Y. Lee can not be used in ALD because of the required performance and character of ALD source chemicals and the location of the reducing agent. If a titanium reducing agent is covered by titanium halide molecules and it is exposed to reactive nitrogen containing source chemical like ammonia a layer of very 10 inert titanium nitride will grow on its surface. Thus the formed titanium nitride layer prevents the desired reduction reaction of  $TiCl_4$  gas pulses.

15

#### Summary of the Invention

It is an object of the present process to eliminate the problems of prior art and to provide a novel method of reducing metal source materials in an ALD type process. It is another object of the invention to provide a novel method of preparing metal nitride thin films by 20 an ALCVD type method.

It is a further object of the present invention to provide an apparatus for growing metal nitride thin films by an ALD type method.

25 These and other objects together with the advantages thereof over known processes are accomplished as hereinafter described and claimed.

The present invention is based on the surprising finding that metal source compounds used in an ALD type process can be reduced at moderate temperatures before being adsorbed or 30 chemisorbed on the surface of a substrate. According to the invention the metal source compounds are therefore conducted in gaseous state into a reduction zone in which they are contacted with a solid or liquid reducing agent maintained at an elevated temperature in order to produce a gaseous reaction product containing the metal species of the metal

source compound at a lower state of oxidation. The reduced metal source material is then contacted with the substrate and deposited on it according to the principles of ALD.

In comparison to the modification method for CVD titanium source chemicals described by  
5 C.-Y. Lee above, the present *in situ* reduction is carried out at low temperatures, in particular at temperatures close to the actual substrate temperature, whereas in the known CVD method, temperatures of 900 °C were used. As the below examples show, the reduction of the metal source material in the reduction zone and the reaction between the metal source material and the metal species bound to and originating from the surface give  
10 rise to gaseous reaction products which easily can be removed from the reduction zone or from the reaction space and which have a sufficiently high vapor pressure for being used as source materials in an ALD process.

Taking titanium chloride as an example, the reduction TiCl<sub>4</sub> at 400 °C gives rise to  
15 titanium subchlorides, such as Ti<sub>2</sub>Cl<sub>6</sub>, which can be transported to the substrate by inert gas. The results are quite surprising, because it has generally been believed that titanium subhalides are not suitable for low-temperature ALD due to low vapor pressure.

The apparatus according to the present invention comprises a reduction zone placed in  
20 contact with both the reaction space and with the sources of metal compounds. Having regard to the flow path of the gaseous reactants which are to be reduced, the reduction zone is placed before the substrate, such that gaseous reactants can be brought into contact with the reduction zone before they are subjected to surface reactions with the substrate. Typical positions are in the flow channel interconnecting the source material containers and the  
25 reaction chambers, and in the reaction chambers upstream from the substrates.

In the present invention the reduction zone is placed before the reaction zone. In the apparatus according to C.-Y. Lee [The Preparation of Titanium-Based Thin Film by CVD Using Titanium Chlorides as Precursors, Chem. Vap. Deposition, 5 (1999) 69 – 73] the  
30 reducing zone and the substrate are located in the same space.

In ALD method the thermal decomposition of the source chemicals is prevented by applying low substrate temperature, thus thermal decomposition of low oxidation state

titanium chlorides to metal state titanium on the substrate and to halogen molecules in the gas phase is prevented.

According to the present invention the reactivity and clean surface of the reducing agent is  
5 ensured by separating the reduction zone and the reaction zone from each other. Thus the metal source chemical pulses contacting the reducing agent always meet a surface capable of changing the oxidation state of the metal source chemicals.

More specifically, the method of reducing a metal source compound is characterized by  
10 what is stated in the characterizing part of claim 1.

The method of growing metal nitride thin films is characterized by what is stated in the characterizing part of claim 10.

15 The apparatus for growing metal thin films on a substrate is characterized by what is stated in the characterizing part of claim 18.

A number of considerable advantages are accomplished with the aid of the invention. The growing rate of the thin film is high, e.g., the growth rate of ALD titanium nitride thin film  
20 increased by almost a factor of 2 compared with the processes of the prior art. In addition, the invention makes it possible to operate at low temperatures. When the reduction of the metal source material is carried out *in situ*, in other words, in the reactor system without using a separate reducing agent pulse, no additional reagent for reduction needs to be introduced into the reaction space. Thus, also one purging step is avoided. This leads to  
25 shorter cycle times and thus to more efficient growing of the films.

The reduction of the metal source material gives lower resistivity to metal nitride film, since the amount of metal increases with respect to the amount of nitrogen. The present process gives as good reduction properties and thus as good film resistivities as the  
30 processes of prior art with a simpler and faster growing procedure.

As mentioned above, the compounds formed as byproducts in the reduction reaction and in the reaction between the metal species on the surface of the substrate are essentially

gaseous and they exit the reactor easily when purging with an inert gas. The amount of residues in the film is on a very low level.

A film grown with the present process exhibits good thin film properties. Thus, the metal  
5 nitride films obtained have an excellent conformality even on uneven surfaces and on  
trenches and vias. The method also provides an excellent and automatic self-control for the  
film growth.

The ALD grown metal nitride films can be used, for example, as ion diffusion barrier  
10 layers in integrated circuits. Tungsten nitride stops effectively oxygen and increases the  
stability of metal oxide capacitors. Transition metal nitrides and especially tungsten nitride  
is also suitable as an adhesion layer for a metal, as a thin film resistor, for stopping the  
migration of tin through via holes and improving the high-temperature processing of  
integrated circuits.

15

Next, the invention is described in detail with the aid of the following detailed description  
and by reference to the attached drawing.

#### Brief Description of the Drawing

20

Figure 1 presents a schematic picture of the preferred arrangement of the present invention.  
Figure 2 illustrates the preferred pulsing sequence in the growing of nitride thin films  
according to the present invention.

25

#### Detailed Description of the Invention

##### **Definitions**

For the purposes of the present invention, an "ALD type process" designates a process in  
30 which deposition of vaporized material onto a surface is based on sequential and  
alternating self-saturating surface reactions. The principles of ALD are disclosed, e.g., in  
US 4 058 430 and 5 711 811.

"Reaction space" is used to designate a reactor or reaction chamber in which the conditions can be adjusted so that deposition by ALD is possible.

"Reduction zone" designates an area or space in which the reducing agent is arranged and over or through which the material to be reduced is conducted to flow.

"Thin film" is used to designate a film which is grown from elements or compounds that are transported as separate ions, atoms or molecules via vacuum, gaseous phase or liquid phase from the source to the substrate. The thickness of the film depends on the application and it varies in a wide range, e.g., from one molecular layer to 800 nm or even up to 1000 nm.

### **The deposition process**

15 According to the present invention metal nitride thin films are prepared by the ALD process. Thus, a substrate placed in a reaction chamber is subjected to alternately repeated surface reactions of at least two vapor-phase reactants for the purpose of growing a thin film thereon. Metal compounds used as source materials for the thin film metal are reduced by a solid or liquid reducing agent when conducted through the reduction zone in which

20 the reducing agent is located. Thereafter, the reduced compounds are deposited on a substrate maintained at an elevated temperature. A subsequently fed pulse of a gaseous or volatile nitrogen source material reacts with the deposited metal species forming a metal nitride.

25 According to the present invention, vapor-phase pulses of the metal source material and the nitrogen source material are preferably fed into the reactor with the aid of an inert carrier gas, such as nitrogen.

30 Preferably, and to make the reaction faster, each feeding pulse is followed by an inert gas pulse to purge the reduction zone and the reaction space, respectively, from unreacted residues of the previous chemical and from the byproducts formed in the reduction and/or the surface reaction. This allows for using highly reactive chemicals and, thus, lower deposition temperatures. The inert gas pulse, also referred to as "gas purge" comprises an inactive gas, such as nitrogen, or a noble gas, such as argon.

Thus, one pulsing sequence (also referred to as a "cycle"), comprising a reduction step, preferably includes the following features:

- providing a vapor-phase pulse of a metal source material;
  - 5 - feeding the vapor-phase metal source pulse into a reduction zone comprising a solid or liquid reducing agent having a low vapor pressure;
  - contacting the metal source material with the reducing agent in order to reduce the metal source material into a reduced gas phase source material pulse;
  - recovering the reduced gas phase source material and conducting it into a reaction
  - 10 chamber;
  - contacting the reduced gas phase material with a substrate surface in order to deposit a metal species on the surface;
  - purging the reaction space with an inert gas;
  - feeding a vapor-phase pulse of a nitrogen source material into the reaction
  - 15 chamber;
  - contacting the nitrogen source material with the metal species on the surface of the substrate in order to form a metal nitride; and
  - purging the reaction space with an inert gas.
- 20 The metal source material flows over the reducing agent and becomes reduced before adsorbing or chemisorbing on a heated substrate surface. The reducing agent is heated to approximately 200 – 800 °C, preferably to 300 – 500 °C. As mentioned above, the reduction temperature is preferably close to the actual deposition temperature. The temperature is dependent on the metal material, for example for the reduction of TiCl<sub>4</sub> on
- 25 Ti, the temperature of the reducing agent is preferably approximately 400 °C, however, preferably lower than the substrate temperature. Deposition of the reduced titanium compound can be carried out at 350 to 400 °C.

A successful reduction process requires that non-reduced source chemical be in gaseous state. The reducing agent has a reactive surface which preferably stays essentially uncontaminated during the process and the reaction products do not accumulate on the surface of the reducing agent. This is facilitated by selecting the metal source material and reducing agent pair so that reduced source chemical has sufficiently high vapor pressure for transporting. In addition, the byproducts of the reduction should preferably have sufficient

vapor pressure to be purged away, and be relatively inert. As a non-limiting example, silicon and boron can react with high oxidation state metal halide gases forming low oxidation state metal halides. Non-metal halide vapors, such as SiF<sub>4</sub>, SiCl<sub>4</sub>, BF<sub>3</sub> and BCl<sub>3</sub>, that are formed in the reactions as by-products can be purged away from the reactor  
5 with an inert gas.

The deposition of the source material(s) on the substrate surface can be carried out at normal pressure, but it is preferred to operate the method at reduced pressure. The pressure in the reaction space is typically 0.01 – 20 mbar, preferably 0.1 – 5 mbar. The substrate  
10 temperature has to be low enough to keep the bonds between metal atoms intact and to prevent decomposition of the gaseous reactants. On the other hand, the substrate temperature has to be high enough to keep the source materials in gaseous phase, i.e., condensation of the gaseous reactants must be avoided. Further, the temperature must be sufficiently high to provide the activation energy for the surface reaction. Depending on the  
15 pressure, the temperature of the substrate is typically 200 – 700 °C, preferably at 250 – 500 °C.

At these conditions, the amount of reactants bound to the surface will be determined by the surface. This phenomenon is called "self-saturation".

20 Maximum coverage on the substrate surface or on the surface of the growing film is obtained when a single layer of reduced metal source chemical molecules or a single layer of nitrogen source chemicals is adsorbed. The pulsing sequence is repeated until a metal nitride film of predetermined thickness is grown.

25 The source temperature is preferably set below the substrate temperature. This is based on the fact that if the partial pressure of the source chemical vapor exceeds the condensation limit at the substrate temperature, controlled layer-by-layer growth of the film is lost.

30 The time available for the self-saturated reactions is limited mostly by economical factors such as required throughput of a product from the reactor. Very thin films are made by relatively few pulsing cycles and, in some cases, this enables an increase of the source chemical pulse times and, thus, utilization of source chemicals with a lower vapor pressure than normally.

The purging time has to be long enough to prevent gas phase reactions and to prevent transition metal nitride thin film growth rates higher than one lattice constant of said nitride per pulsing sequence.

5

### Reducing agents

The reducing agent is preferably solid. Most suitable are elemental reducing agents, either metals or reactive non-metals. According to a preferred embodiment of the invention the 10 reducing agent is a metal, preferably the same metal as the metal component of the source material, but naturally it is possible to use some other suitable reducing metal as well. The metal is preferably a transition metal of group 4, 5 or 6, i.e., Ti, Zr, Hf, V, Nb, Ta, Cr, Mo or W. The reactive non-metals preferably used as reducing agents comprise B, Si, Ge and P. It is also possible to employ some reactive metal compounds, such as metal silicides or 15 germanides as reducing agents. Silicon and germanium halides typically formed as byproducts in the reduction are volatile and can be purged away from the reducing zone.

The reducing agent can, however, be liquid. It is important that the vapor pressure of the liquid reducing agent is low so that it will not enter into the reaction space and hamper the 20 reactions of the source materials with the substrate surface. An example of a suitable liquid reducing agent is gallium metal, which melts at approximately 30 °C and has a boiling point of approximately 2400 °C.

### The reactor system

25

Generally, the apparatus according to the present invention can be any type of an ALD reactor to which a reduction zone comprising the solid reduction agent has been added. Such an apparatus typically comprises reaction space into which the substrate can be placed, e.g. on a holder or jig, and at least one inlet flow channel which can be connected 30 to a metal source material container for allowing feed of a metal source material in the form of vapor-phase pulses from a metal source material container into the reaction space. There is typically also at least one outlet flow channel connected to the reaction space for removal of gas phase reaction products. According to the present invention, a reactor of the

above described construction is modified by incorporating a reduction zone at a point along the gas flow path of the gaseous reactant.

A schematic picture of the preferred reduction arrangement according to the present invention is depicted in Figure 1. According to this preferred arrangement, the reduction zone is located between the metal source material container and the substrate of the reaction space. The nitrogen source material can be fed to the reaction space either through the same flow channel or through a different flow channel. The nitrogen source material is not reduced in the reduction zone.

10

Typically the reduction zone is located in the gas flow channel situated between the source material stock container and the reaction space, preferably just before the reaction space (also referred to as substrate chamber). In such an arrangement, the reducing agent is typically present in the form of a cartridge. It is also possible to coat the flow channel leading from the metal source material stock container to the reaction space with reducing material. In such an arrangement, the flow channel is then heated to a temperature which is needed for the reduction reaction of the source material to take place, for example, for titanium at approximately 350 – 400 °C.

20 Another embodiment of the invention comprises fitting the reducing agent into the reaction space, essentially upstream to the substrate. In such an arrangement the reducing agent is typically shaped as a monolithic block.

In both cases it is important to be able to remove the reducing agent and/or the container  
25 thereof for regeneration and/or refill as easily as possible.

#### **Substrate materials**

The substrate can be of various types. Examples include silicon, silica, coated silicon and  
30 copper metal. The present film-growing process provides an excellent method for growing of conformal layers in geometrically challenging applications.

#### **Metal source materials**

The invention can be applied especially to the reduction of transition metal chemicals, i.e., elements of groups 3, 4, 5, 6, 7, 8, 9, 10, 11 and/or 12 (according to the system recommended by IUPAC) in the periodic table of elements, because these metals can form compounds of several different oxidation states. In particular, the deposited film consists 5 essentially of W, Ti, Zr, Hf, V, Nb, Ta, Cr, and/or Mo nitride(s) and, thus, gaseous or volatile compounds of these are preferably used in the method of the present invention.

Particularly preferred are compounds of tungsten and titanium. Preferably, a tungsten source material is used.

10 Since the properties of each metal compound vary, the suitability of each metal compound for the use in the process of the present invention has to be considered. The properties of the compounds are found, e.g., in N. N. Greenwood and A. Earnshaw, Chemistry of the Elements, 1<sup>st</sup> edition, Pergamon Press, 1986.

15 The metal source material (as well as the reducing boron compound and the nitrogen source material) has to be chosen so that requirements for sufficient vapor pressure, the above-discussed criteria of sufficient thermal stability at substrate temperature and sufficient reactivity of the compounds are fulfilled.

20 Sufficient vapor pressure means that there must be enough source chemical molecules in the gas phase near the substrate surface to enable fast enough self-saturated reactions at the surface.

25 In practice sufficient thermal stability means that the source chemical itself must not form growth-disturbing condensable phases on the substrates or leave harmful levels of impurities on the substrate surface through thermal decomposition. Thus, one aim is to avoid non-controlled condensation of molecules on substrates.

30 Further selecting criteria may include the availability of the chemical in a high purity, and the easiness of handling, inter al., reasonable precautions.

In addition, the quality of the products of the reduction reaction and its byproducts needs to be considered, since the controlled process is lost if an inert metal boride, phosphide or

carbide layer is formed on the reducing agent. Thus, it is important that the reaction product be essentially gaseous. By this it is meant that the compound formed is gaseous enough to be moved from the reaction space with the aid of the inert purging gas, which means that they will not remain as impurities on the reducing agent or in the films.

5

Typically suitable metal source materials can be found among halides, preferably fluorides, chlorides, bromides or iodides, or metal organic compounds, preferably alkylaminos, cyclopentadienyls, dithiocarbamates or betadiketonates of desired metal(s).

- 10 Most common volatile transition metal halides of groups 4, 5 and 6 of the periodic table of elements that have potential as source chemicals for the reduction method are  $TiCl_4$ ,  $TiBr_4$ ,  $TiI_4$ ,  $ZrCl_4$ ,  $ZrBr_4$ ,  $ZrI_4$ ,  $HfCl_4$ ,  $HfBr_4$ ,  $HfI_4$ ,  $WF_6$ ,  $WCl_6$ ,  $WBr_6$ ,  $TaF_5$ ,  $TaCl_5$ ,  $TaBr_5$ ,  $NbF_5$ ,  $NbCl_5$ ,  $NbBr_5$ ,  $VF_5$  and  $VCl_4$ .
- 15 According to a preferred embodiment transition metal nitrides are mixed so that in the growing process two or more different metal source materials are used. For example, tungsten nitride can be mixed with titanium nitride.

- 20 The reduced metal reactant will react with the substrate surface forming a (covalent) bond to the surface bonding groups. The adsorbed metal species will contain a residue of the reactant compound, such as a halogen or hydrocarbon. It is assumed that this residue reacts with a nitrogen-containing compound.

#### Nitrogen materials

25

The nitrogen compound used as the nitrogen source material is volatile or gaseous and chosen bearing in mind the same criteria as for the metal source material. In general, the nitrogen compound can be any volatile, thermally sufficiently stable nitrogen compound capable of reacting with the metal species bound on the surface at the reaction conditions.

30

The reactions of different metal source materials with one and same nitrogen source material (and vice versa) can lead to different reaction (by)products. According to the present invention, the metal source material and nitrogen source material are selected so that the resulting byproduct(s) is (are) gaseous. By this it is meant that the compound

formed is gaseous enough to be moved from the reaction space with the aid of the inert purging gas, and, on the other hand, does not catalytically decompose to condensable species. According to the present invention, byproducts will not remain as impurities in the films. If a reactive site on the surface is contaminated, the growing rate of the film 5 decreases. By selecting the metal source material(s) and boron compound as indicated above, the growing rate of the film does not essentially decrease, i.e., decreases by a maximum of 0.1%, preferably by less than 0.01%, and in particular by less than 0.001% in each cycle.

10 The selection can be facilitated with computer programs having a sufficiently extensive thermodynamics database, which enables to check the reaction equilibrium and thus predict which reactants have thermodynamically favourable reactions. An example of this kind of programs is HSC Chemistry, version 3.02 (1997) by Outokumpu Research Oy, Pori, Finland.

15

Preferably, the nitrogen compound is selected from the group comprising

- ammonia ( $\text{NH}_3$ ) and its salts, preferably halide salt, in particular ammonium fluoride or ammonium chloride;
- hydrogen azide ( $\text{HN}_3$ ) and the alkyl derivates of the said compound such as 20  $\text{CH}_3\text{N}_3$ ;
- hydrazine ( $\text{N}_2\text{H}_4$ ) and salts of hydrazine such as hydrazine hydrochloride;
- alkyl derivates of hydrazine such as dimethyl hydrazine;
- nitrogen fluoride  $\text{NF}_3$ ;
- hydroxyl amine ( $\text{NH}_2\text{OH}$ ) and its salts such as hydroxylamine hydrochloride;
- 25 - primary, secondary and tertiary amines such as methylamine, diethylamine and triethylamine; and
- nitrogen radicals such as  $\text{NH}_2^{**}$ ,  $\text{NH}^{**}$  and  $\text{N}^{***}$ , in which \* means a free electron capable of bonding, and excited state of nitrogen ( $\text{N}_2^*$ ).

30 The following non-limiting examples illustrate the invention:

#### EXAMPLE 1

Experiments were performed with an F200 ALD reactor, as described in Finnish Patent No. 100409 of assignee by Suntola et al. Two series of titanium nitride samples were produced. One series of samples was made from  $TiCl_4$  and  $NH_3$ . Heated reactor parts in contact with metal halides were passivated with amorphous aluminium oxide which protected the parts against corrosion.  $TiCl_4$  was evaporated from a source bottle at room temperature. The source gas was carried to the substrate chamber by nitrogen gas. Purging with nitrogen gas removed surplus  $TiCl_4$  molecules from the reactor. Then an  $NH_3$  gas pulse was introduced to the substrate chamber. The pulsing cycle was ended with a nitrogen purge which removed surplus  $NH_3$  and gaseous reaction byproducts from the reactor. The pulsing cycle was repeated 1000 times. The pressure of the substrate chamber was in the range of 200 - 1000 Pa. The resulting thin film on silicon wafer had metallic lustre with a yellowish hue. The growth rate at 400 °C was 0.17 Å/cycle.

Another series of samples was grown from  $TiCl_4$  and  $NH_3$  with titanium metal (referred to as TiN-Ti hereinafter).  $TiCl_4$  was evaporated from a source bottle at room temperature. The  $TiCl_4$  vapor was carried towards the substrate chamber by nitrogen gas. In the gas flow channel near the substrate chamber there was titanium metal heated to 400 °C.  $TiCl_4$  flowed over titanium metal and the reaction products denoted with  $TiCl_x$  were carried to the substrate chamber by nitrogen gas. Nitrogen purge removed surplus  $TiCl_x$  molecules from the substrate chamber. Then  $NH_3$  gas pulse was introduced to the substrate chamber. The pulsing cycle was ended with a nitrogen purge which removed surplus  $NH_3$  and gaseous reaction byproducts from the reactor. The pulsing cycle was repeated 1000 times. The resulting thin film on silicon wafer had metallic lustre with a yellowish hue. The thickness of the thin film was measured by Electron Diffraction Spectroscopy (referred to as EDS hereinafter). A growth rate was calculated by dividing the thickness by the number of pulsing cycles. The growth rate of the TiN-Ti film at 400 °C (0.31 Å/cycle) was almost doubled compared to TiN samples (0.17 Å/cycle) that were grown with equal deposition parameters without titanium metal. There was chlorine in the films as an impurity but the concentration stayed below 1.5 wt.-%. When the growth temperature was decreased from 400 °C to 350 °C, the amount of chlorine increased to 4.0 wt.-% and the resistivity increased from 200  $\mu\Omega cm$  to 450  $\mu\Omega cm$ . Using titanium metal did not affect the chlorine content of the film.

Exact reactions of  $TiCl_4$  on titanium metal and the composition of the resulting  $TiCl_x$  source chemical vapor are to be argued. One possible reaction, which is thermodynamically favourable, is presented in Eq. 1. A dimer  $(TiCl_3)_2$  or written as  $Ti_2Cl_6$  which chemisorbs on substrate surface may explain the increased growth rate of the 5 nitride film. If the number of reactive surface sites (e.g.  $-NH_2$  and  $=NH$  groups) on TiN and TiN-Ti is the same, molecules with higher metal / halide ratio will add more metal per pulsing cycle on the surface than metal compounds of high oxidation state. The reaction equation (Eq. 2), which describes the nitride formation, is thermodynamically favourable. The free Gibbs energy value must be assessed with care because data regarding adsorbed 10 molecules was not available for calculations.



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#### EXAMPLE 2

The same ALD reactor as in Example 1 was used for the reduction experiment.  $WF_6$  was evaporated from a source bottle at room temperature and carried towards the substrate 20 chamber by nitrogen gas. In the gas flow channel near the substrate chamber there was tungsten metal foil heated to  $400\text{ }^{\circ}C$ .  $WF_6$  flowed over tungsten metal, and the assumed reaction products (denoted with  $WF_x$ ) were carried to the substrate chamber by nitrogen gas. However, it was not possible to detect any visual signs of corrosion on W metal after the experiment. Theoretical calculations confirmed that at least simple reactions Eq. 3 and 25 Eq. 4 are not favourable thermodynamically.



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#### THEORETICAL EXAMPLE 3

Tungsten hexafluoride ( $WF_6$ ) is evaporated from the source bottle and carried towards the substrate chamber by nitrogen gas. Along the gas route there is a cartridge filled with

tungsten silicide pieces. The cartridge is heated to 400 °C. The reduction of WF<sub>6</sub> into WF<sub>4</sub> is thermodynamically favourable (Eq. 5). The pulsing sequence in the point of substrate is as follows: WF<sub>x</sub> vapor pulse / N<sub>2</sub> gas purge / NH<sub>3</sub> vapor pulse / N<sub>2</sub> gas purge.



It can be argued whether SiF<sub>4</sub> disturbs the thin film growth process. However, experiments with ALE have shown that it is very difficult to grow any silicon oxide or silicon nitride film from silicon halides. SiF<sub>4</sub> molecules may have low reactivity with NH<sub>3</sub> gas and they  
10 can be purged away with nitrogen.

#### EXAMPLE 4

The effect of tungsten on the on the growth of titanium nitride thin film was experimented  
15 in an ALD reactor similar to the ones used in Examples 1 and 2. Heated source vapor flow channels before the reaction chamber were coated with tungsten metal. Titanium nitride deposition cycle consisted of the following steps: TiCl<sub>4</sub> vapor pulse/N<sub>2</sub> gas purge/NH<sub>3</sub> vapor pulse/N<sub>2</sub> gas purge. The deposition cycle was repeated 500 times. Source chemical vapor pulses flowed through the tungsten-coated flow channels at 350 – 400 °C. The thin  
20 film deposited at 350 and 400 °C had improved growth rate and decreased resistivity compared to samples grown without the use of tungsten metal. According to the electron diffraction spectroscopy (EDS) the thin film consisted of titanium and nitrogen. No tungsten in the film was found by EDS.

**Claims:**

1. A method of reducing transition metal source materials in an ALD type process, characterized by the steps of
  - 5      – vaporizing a metal source material,
  - conducting the vaporized metal source material, optionally with the aid of an inert carrier gas, into a reducing zone comprising a solid or liquid reducing agent maintained at an elevated temperature,
  - contacting the metal source material with the solid or liquid reducing agent in  
10     order to convert the source material into a reduced metal compound and reaction byproducts having a sufficiently high vapor pressure for transporting in gaseous form,
  - recovering the reduced metal compound and using it as a gaseous reactant in an ALD process.
- 15     2. The method according to claim 1, wherein the reducing agent is a metal.
3. The method according to claim 2, wherein the metal is selected from the group comprising Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W.
- 20     4. The method according to claim 2 or 3, wherein the reducing agent metal is the same as in the metal source compound.
5. The method according to claim 2 or 3, wherein the reducing agent metal is different  
25     from the metal in the metal source compound.
6. The method according to claim 1, wherein the reducing agent is a reactive non-metal or metal compound.
- 30     7. The method according to claim 6, wherein the reducing agent is selected from the group comprising B, Si, Ge, P, and metal silicides and metal germanides.

8. The method according to any of the preceding claims, wherein the reduction of the metal source material is carried out in a reduction zone located in a flow channel between metal source chemical stock container and the reaction space.

5 9. The method according to any of claims 1 – 7, wherein the reduction of the metal source material is carried out at a temperature close to the growth temperature of the ALD process.

10. A process for producing transition metal nitride thin films on a substrate by an ALD type process, wherein alternating vapor-phase pulses of

- 10     – at least one metal source material, and  
      – at least one nitrogen source material capable of reacting with the reduced metal source material bound to the substrate and forming gaseous reaction byproducts in the reaction,

are fed to a reaction space and contacted with the surface of the substrate,

15 characterized by

- subjecting the metal source material to reduction prior to deposition thereof on the substrate.

11. The method according to claim 10, wherein the process consists essentially of growing 20 the transition metal nitride thin films by repeating a pulsing sequence, which comprises

- 20     – providing a vapor-phase pulse of a metal source material;  
      – feeding the vapor-phase metal source pulse into a reduction zone comprising a solid or liquid reducing agent;  
      – contacting the metal source material with the reducing agent in order to reduce the 25 metal source material into a reduced gas phase source material pulse;  
      – recovering the reduced gas phase source material and conducting it into a reaction chamber;  
      – contacting the reduced gas phase material with a substrate surface in order to deposit a metal species on the surface;  
30     – purging the reaction space with an inert gas;  
      – feeding a vapor-phase pulse of a nitrogen source material into the reaction chamber;  
      – contacting the nitrogen source material with the metal species on the surface of the substrate in order to form a metal nitride; and

- purging the reaction space with an inert gas.

12. The method according to claim 10 or 11, wherein the reduction of the metal source compound is carried out by conducting the vaporized metal source material over a solid or  
5 liquid reducing agent maintained at an elevated temperature.

13. The method according to claim 10, wherein the metal source material is the compound of a transition metal compound, preferably a transition metal of group 4 (Ti, Zr, Hf), 5 (V, Nb, Ta) or 6 (Cr, Mo, W) of the periodic table of elements.

10

14. The method according to claim 13, wherein the metal compounds are halides, preferably fluorides, chlorides, bromides or iodides, or metal organic compounds, preferably alkylaminos, cyclopentadienyls, dithiocarbamates and/or betadiketonates.

15

15. The method according to claim 13 or 14, wherein the metal source material is titanium halide, preferably  $TiCl_4$ .

16. The method according to claim 10, wherein the nitrogen source material is selected from the group comprising

20

- ammonia ( $NH_3$ ) and its salts, preferably halide salt, in particular ammonium fluoride or ammonium chloride;
- hydrogen azide ( $HN_3$ ) and the alkyl derivates thereof, preferably  $CH_3N_3$ ;
- hydrazine ( $N_2H_4$ ) and salts of hydrazine such as hydrazine hydrochloride;
- alkyl derivates of hydrazine, preferably dimethyl hydrazine;

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- nitrogen fluoride  $NF_3$ ;
- hydroxyl amine ( $NH_2OH$ ) and salts thereof, preferably hydroxylamine hydrochloride;
- primary, secondary and tertiary amines, preferably methylamine, diethylamine and triethylamine; and

30

- nitrogen radicals such as  $NH_2^*$ ,  $NH^{**}$ ,  $N^{***}$ , in which \* means a free electron capable of bonding, and excited state of nitrogen ( $N_2^*$ ).

17. The method according to claim 10, wherein the transition metal nitride thin film is used as a diffusion barrier in integrated circuits.

18. An apparatus for growing thin films on a substrate by an ALD type process, comprising
- a reaction space into which the substrate can be placed, and
  - a flow channel connected to the reaction space and which can be connected to a metal source material container for feeding metal source material in the form of vapor-phase pulses from the metal source material container into the reaction space,
- 5 characterized by a
- a reducing zone including a solid or liquid reducing agent, arranged along the flow path of the vapor-phase pulses of the metal source material at a point in between the metal source material container and the reaction space for contacting the metal source material with the reducing agent prior to bringing the metal source material into contact with the substrate.
- 10
- 15 19. The apparatus according to claim 18, wherein the apparatus comprises at least two source material containers and/or at least one inert gas source connected to the flow channel.
- 20
20. The apparatus according to claim 18 or 19, wherein the apparatus comprises at least two inlet flow channels connectable to at least two source material containers and/or at least one inert gas source.
- 25
21. The apparatus according to claim 18, wherein the reducing zone is in the form of a cartridge located in the flow channel.
22. The apparatus according to claim 21, wherein the reducing zone is the flow channel or a part of it coated with the reducing agent.

1/2

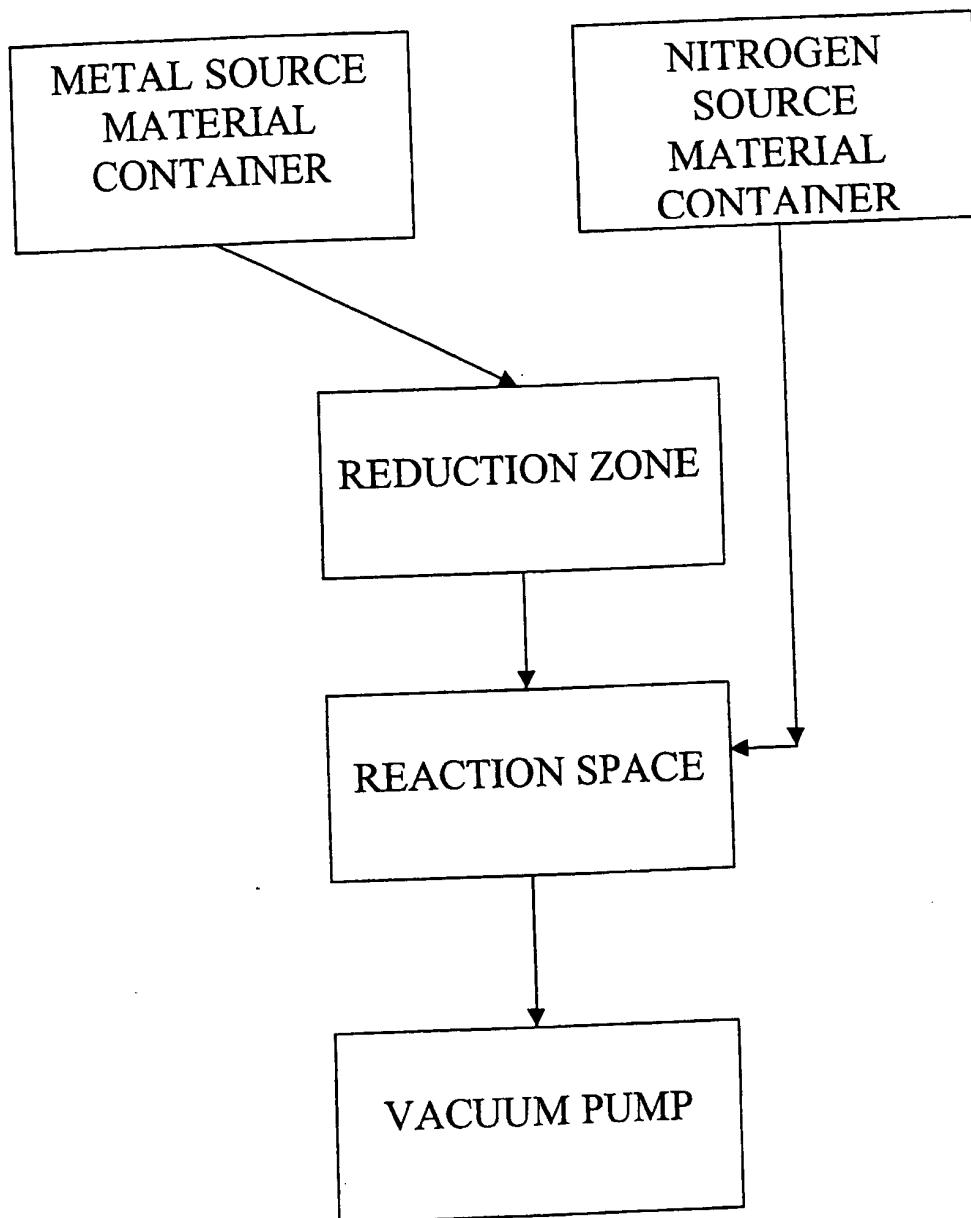


Fig. 1

2/2

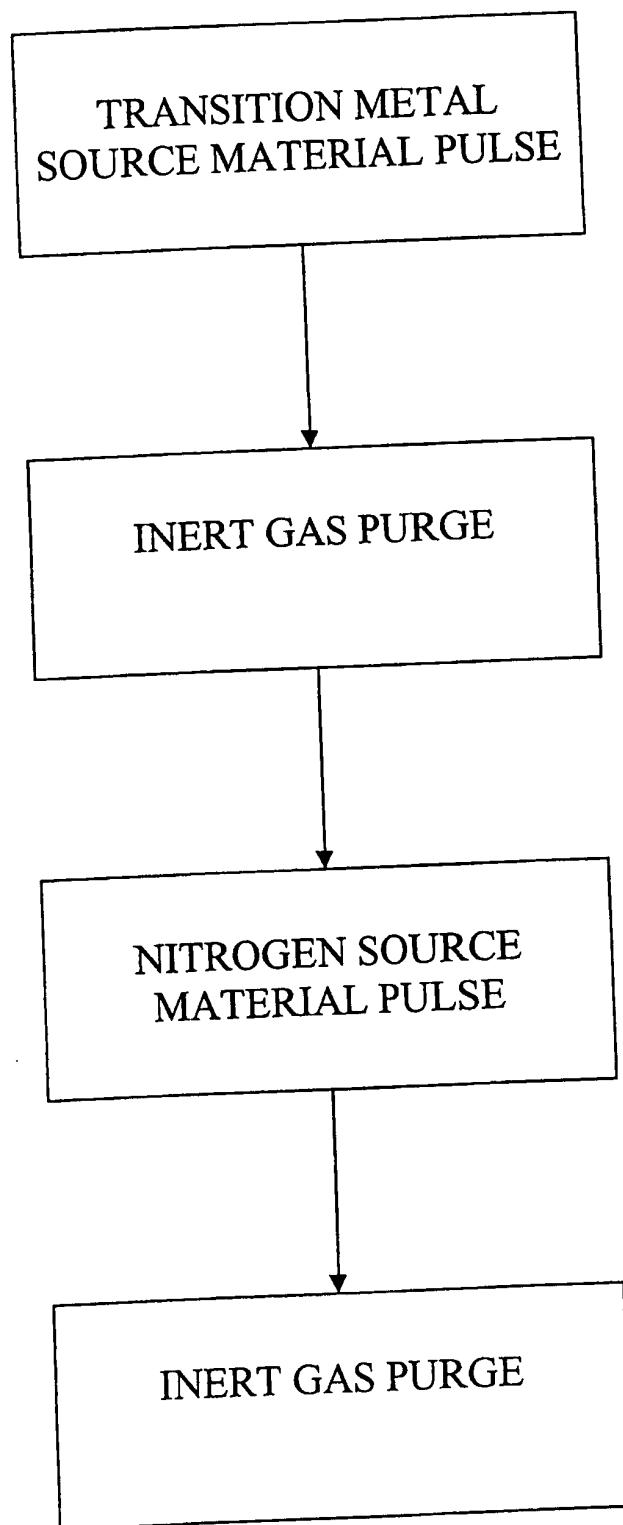


Fig. 2

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/FI 00/00884

## A. CLASSIFICATION OF SUBJECT MATTER

**IPC7: C23C 16/44, C23C 16/00, C30B 25/02, C30B 35/00**  
According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

**IPC7: C23C, C30B, H01L**

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

**SE,DK,FI,NO classes as above**

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHEMICAL VAPOR DEPOSITION, Volume 5, No 2, March 1999, Chi-Young Lee, "The Preparation of Titanium-Based Thin Film by CVD Using Titanium Chlorides as Precursors" page 69 - page 73 --	1-9,18-22
X	J. ELECTROCHEM. SOC., Volume 142, No 8, August 1995, Mikko Ritala et al, "Atomic Layer Epitaxy Growth of TiN Thin Films" page 2731 - page 2737 --	10,12-17
X	APPLIED SURFACE SCIENCE, Volume 82/83, 1994, Kai-Erik Elers et al, "NbC15 as a precursor in atomic layer epitaxy", page 468 - page 474, see especially page 469 - page 471 and 473 -----	10,12-17

Further documents are listed in the continuation of Box C.

See patent family annex.

\* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier application or patent but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed
- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search

**16 January 2001**

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**Basic Patent (Number,Kind,Date): FI 200000564 A0 20000310**

**Patent Family:**

Patent Number	Kind	Date	Application Number	Kind	Date
AU 200068003	A5	20010319	AU 200068003	A	20000824
AU 200079257	A5	20010423	AU 200079257	A	20001012
AU 200079268	A5	20010423	AU 200079268	A	20001013
AU 200110884	A5	20010430	AU 200110884	A	20001016
AU 200112082	A5	20010430	AU 200112082	A	20001016
FI 9902233	A	20010416	FI 992233	A	19991015
FI 9902234	A	20010416	FI 992234	A	19991015
FI 9902235	A	20010416	FI 992235	A	19991015
FI 200000564	A	20010416	FI 2000564	A	20000310
FI 200000564	A0	20000310	FI 2000564	A	20000310 (Basic)
WO 200115220	A1	20010301	WO 2000US23252	A	20000824
WO 200127346	A1	20010419	WO 2000FI884	A	20001012
WO 200127347	A1	20010419	WO 2000FI895	A	20001013
WO 200129280	A1	20010426	WO 2000US28537	A	20001016
WO 200129891	A1	20010426	WO 2000US23213	A	20000824
WO 200129893	A1	20010426	WO 2000US28654	A	20001016

**Priority Data:**

Patent Number	Kind	Date
US 150486	P	19990824
US 159799	P	19991015
US 176944	P	20000118
WO 2000US23252	W	20000824
FI 992233	A	19991015
WO 2000FI884	W	20001012
FI 992234	A	19991015
WO 2000FI895	W	20001013
FI 992235	A	19991015
FI 2000564	A	20000310
US 176948	P	20000118
WO 2000US28537	W	20001016
US 175799	P	19991015

**PATENT FAMILY:** **Australia (AU)**

Patent (Number,Kind,Date): AU 200068003 A5 20010319

METHOD FOR BOTTOMLESS DEPOSITION OF BARRIER LAYERS IN INTEGRATED CIRCUIT METALLIZATION SCHEMES (English)

Patent Assignee: ASM INC

Author (Inventor): SATTA ALESSANDRA; MAEX KAREN; ELERS KAI-ERIK; SAANILA VILLE ANTERO; SOININEN PEKKA JUHA; HAUKKA SUVI P

Priority (Number,Kind,Date): US 150486 P 19990824; US 159799 P 19991015; US 176944 P 20000118; WO 2000US23252 W 20000824

Applic (Number,Kind,Date): AU 200068003 A 20000824

IPC: \* H01L-021/768; H01L-023/532; H01L-021/285; C23C-016/00

CA Abstract No: \* 134(13)187114R; 134(21)304079W; 134(22)318948R

Derwent WPI Acc No: \* C 01-218475

Language of Document: English

Patent (Number,Kind,Date): AU 200079257 A5 20010423

METHOD OF MODIFYING SOURCE CHEMICALS IN AN ALD PROCESS (English)

Patent Assignee: ASM MICROCHEMISTRY OY

Author (Inventor): ELERS KAI-ERIK

Priority (Number,Kind,Date): FI 992233 A 19991015; WO 2000FI884 W 20001012

Applic (Number,Kind,Date): AU 200079257 A 20001012

IPC: \* C23C-016/44; C23C-016/00; C30B-025/02; C30B-035/00

CA Abstract No: \* 134(21)303341P; 134(21)304215N; 134(22)318948R

Language of Document: English

 **Patent (Number,Kind,Date): AU 200079268 A5 20010423**

METHOD OF DEPOSITING TRANSITION METAL NITRIDE THIN FILMS (English)

Patent Assignee: ASM MICROCHEMISTRY OY

Author (Inventor): ELERS KAI-ERIK; HAUKKA SUVI PAIVIKKI; SAANILA VILLE ANTERO;

KAPIO SARI JOHANNA; SOININEN PEKKA JUHA

Priority (Number,Kind,Date): FI 992234 A 19991015; WO 2000FI895 W 20001013

Applic (Number,Kind,Date): AU 200079268 A 20001013

IPC: \* C23C-016/44; C23C-016/00; C30B-025/02; H05K-003/00

CA Abstract No: \* 134(21)303342Q; 134(21)304215N; 134(22)318948R

Language of Document: English

Patent (Number,Kind,Date): AU 200110884 A5 20010430

DEPOSITION OF TRANSITION METAL CARBIDES (English)

Patent Assignee: ASM INC

Author (Inventor): ELERS KAI-ERIK; HAUKKA SUVI P; SAANILA VILLE ANTERO; KAPIO SARI

JOHANNA; SOININEN PEKKA JUHA

Priority (Number,Kind,Date): FI 992233 A 19991015; FI 992234 A 19991015; FI 992235 A

19991015; FI 2000564 A 20000310; US 159799 P 19991015; US 176948 P 20000118; WO

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Applic (Number,Kind,Date): AU 200110884 A 20001016

IPC: \* C23C-016/32; H01L-021/00

CA Abstract No: \* 134(13)187114R; 134(21)303341P; 134(21)303342Q; 134(21)304079W; 134(21)304215N; 134(22)318948R

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Language of Document: English

Patent (Number,Kind,Date): AU 200112082 A5 20010430

METHOD FOR DEPOSITING NANOLAMINATE THIN FILMS ON SENSITIVE SURFACES (English)

Patent Assignee: ASM INC

Author (Inventor): ELERS KAI-ERIK; HAUKKA SUVI P; SAANILA VILLE ANTERO; KAIPIO SARI  
JOHANNA; SOININEN PEKKA JUHA

Priority (Number,Kind,Date): FI 992233 A 19991015; FI 992234 A 19991015; FI 992235 A  
19991015; FI 2000564 A 20000310; US 175799 P 19991015; US 176948 P 20000118; WO  
2000US28654 W 20001016

Applic (Number,Kind,Date): AU 200112082 A 20001016

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CA Abstract No: \* 134(21)303341P; 134(21)303342Q; 134(21)304215N; 134(22)318948R

Derwent WPI Acc No: \* C 01-308262; C 01-308263

Language of Document: English

### **Finland (FI)**

Patent (Number,Kind,Date): FI 9902233 A 20010416

MENETELMAE LAEHDEKEMIKAALIEN MUUNTAMISEksi ALCVD-PROSESSISSA  
FOERFARANDE FOER MODIFIERING AV UTGAANGSAEMNESKEMIKALIERNA I EN ALCVD-  
PROSESS (Swedish)

Patent Assignee: ASM MICROCHEMISTRY LTD (FI)

Author (Inventor): ELERS KAI-ERIK (FI)

Priority (Number,Kind,Date): FI 992233 A 19991015

Applic (Number,Kind,Date): FI 992233 A 19991015

IPC: \* C23C-016/44

Language of Document: Finnish; Swedish

Patent (Number,Kind,Date): FI 9902234 A 20010416

MENETELMAE SIIRTYMAEMETALLINITRIDOHUTKALVOJEN KERROSTAMISEksi

FOERFARANDE FOER FRAMSTAELLNING AV OEVERGAANGSMETALLNITRIDTUNNFILMER  
(Swedish)

Patent Assignee: ASM MICROCHEMISTRY LTD (FI)

Author (Inventor): ELERS KAI-ERIK (FI); HAUKKA SUVI (FI); SAANILA VILLE (FI); KAIPIO  
SARI (FI); SOININEN PEKKA (FI)

Priority (Number,Kind,Date): FI 992234 A 19991015

Applic (Number,Kind,Date): FI 992234 A 19991015

IPC: \* C23C-016/44; C30B-025/02

Language of Document: Finnish; Swedish

Patent (Number,Kind,Date): FI 9902235 A 20010416

MENETELMAE ALKUAINEOHUTKALVOJEN KASVATTAMISEksi FOERFARANDE FOER  
FRAMSTAELLNING AV ELEMENTTUNNFILMER (Swedish)

Patent Assignee: ASM MICROCHEMISTRY LTD (FI)

Author (Inventor): ELERS KAI-ERIK (FI); SAANILA VILLE (FI); KAIPIO SARI (FI); SOININEN  
PEKKA (FI)

Priority (Number,Kind,Date): FI 992235 A 19991015

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IPC: \* C23C-016/44; C30B-025/02

Language of Document: Finnish; Swedish

Patent (Number,Kind,Date): FI 200000564 A 20010416

MENETELMAE NANOLAMINAATTIEN VALMISTAMISEksi FOERFARANDE FOER  
FRAMSTAELLNING AV NANOLAMINATER (Swedish)

Patent Assignee: ASM MICROCHEMISTRY OY (FI)

Author (Inventor): ELERS KAI-ERIK (FI); SAANILA VILLE (FI); KAIPIO SARI (FI); SOININEN  
PEKKA (FI)

Priority (Number,Kind,Date): FI 2000564 A 20000310; FI 992233 A 19991015; FI 992234 A

19991015; FI 992235 A 19991015

Applic (Number,Kind,Date): FI 2000564 A 20000310

IPC: \* C23C-016/30

Language of Document: Finnish; Swedish

Patent (Number,Kind,Date): FI 200000564 A0 20000310

MENETELMAE NANOLAMINAATTIEN VALMISTAMISEKSI FOERFARANDE FOER  
FRAMSTAELLNING AV NANOLAMINATER (Swedish)

Patent Assignee: ASM MICROCHEMISTRY OY (FI)

Author (Inventor): ELERS KAI-ERIK (FI); SAANILA ANTERO VILLE (FI); KAIPIO JOHANNA  
SARI (FI); SOININEN JUHA PEKKA (FI)

Priority (Number,Kind,Date): FI 2000564 A 20000310; FI 992233 A 19991015; FI 992234 A  
19991015; FI 992235 A 19991015

Applic (Number,Kind,Date): FI 2000564 A 20000310

IPC: \* C25D

Language of Document: Finnish; Swedish

### World Intellectual Property Organization, PCT (WO)

Patent (Number,Kind,Date): WO 200115220 A1 20010301

METHOD FOR BOTTOMLESS DEPOSITION OF BARRIER LAYERS IN INTEGRATED CIRCUIT  
METALLIZATION SCHEMES (English)

Patent Assignee: ASM INC (US); SATTA ALESSANDRA (BE); MAEX KAREN (BE); ELERS KAI  
ERIK (FI); SAANILA VILLE ANTERO (FI); SOININEN PEKKA JUHA (FI); HAUCCA SUIVI P (FI)

Author (Inventor): SATTA ALESSANDRA (BE); MAEX KAREN (BE); ELERS KAI-ERIK (FI);  
SAANILA VILLE ANTERO (FI); SOININEN PEKKA JUHA (FI); HAUCCA SUIVI P (FI)

Priority (Number,Kind,Date): US 150486 P 19990824; US 159799 P 19991015; US 176944 P  
20000118

Applic (Number,Kind,Date): WO 2000US23252 A 20000824

Designated States: (National) AE; AG; AL; AM; AT; AU; AZ; BA; BB; BG; BR; BY; BZ; CA; CH; CN;  
CR; CU; CZ; DE; DK; DM; DZ; EE; ES; FI; GB; GD; GE; GH; GM; HR; HU; ID; IL;  
IN; IS; JP; KE; KG; KP; KR; LZ; LR; LS; LT; LU; LV; MA; MD; MG; MK; MN; MW; MX; MZ;  
NO; NZ; PL; PT; RO; RU; SD; SE; SG; SI; SK; SL; TJ; TM; TR; TT; TZ; UA; UG; US; UZ; VN;  
ZA; ZW (Regional) GH; GM; KE; LS; MW; MZ; SD; SL; SZ; TZ; UG; ZW; AM; AZ; BY; KG; KZ; MD;  
RU; TJ; TM; AT; BE; CH; CY; DE; DK; ES; FI; FR; GB; GR; IE; IT; LU; MC; NL; PT; SE; BF; BJ; CF; CG;  
CI; CM; GA; GN; GW; ML; MR; NE; SN; TD; TG

Filing Details: WO 130000 With international search report; Before expiration of time limit for amending  
the claims and to be republished in the event of the receipt of the amendments

IPC: \* H01L-021/768; H01L-023/532; H01L-021/285; C23C-016/00

CA Abstract No: \* 134(13)187114R; 134(21)304079W; 134(22)318948R; 134(13)187114R

Derwent WPI Acc No: \* C 01-218475; C 01-328500; C 01-328533; C 01-218475

Language of Document: English

Patent (Number,Kind,Date): WO 200127346 A1 20010419

METHOD OF MODIFYING SOURCE CHEMICALS IN AN ALD PROCESS (English)

Patent Assignee: ASM MICROCHEMISTRY OY (FI); ELERS KAI ERIK (FI)

Author (Inventor): ELERS KAI-ERIK (FI)

Priority (Number,Kind,Date): FI 992233 A 19991015

Applic (Number,Kind,Date): WO 2000FI884 A 20001012

Designated States: (National) AE; AG; AL; AM; AT; AU; AZ; BA; BB; BG; BR; BY; BZ; CA; CH;  
CN; CR; CU; CZ; DE; DK; DM; DZ; EE; ES; FI; GB; GD; GE; GH; GM; HR; HU; ID;  
IL; IN; IS; JP; KE; KG; KP; KR; LZ; LR; LS; LT; LU; LV; MA; MD; MG; MK; MN; MW; MX;  
MZ; NO; NZ; PL; PT; RO; RU; SD; SE; SG; SI; SK; SL; TJ; TM; TR; TT; TZ; UA; UG; US; UZ; VN;  
ZA; ZW (Regional) GH; GM; KE; LS; MW; MZ; SD; SL; SZ; TZ; UG; ZW; AM; AZ; BY; KG; KZ;

MD; RU; TJ; TM; AT; BE; CH; CY; DE; DK; ES; FI; FR; GB; GR; IE; IT; LU; MC; NL; PT; SE; BF; BJ; CF; CG; CI; CM; GA; GN; GW; ML; MR; NE; SN; TD; TG

Filing Details: WO 100000 With international search report

IPC: \* C23C-016/44; C23C-016/00; C30B-025/02; C30B-035/00

CA Abstract No: \* 134(21)303341P; 134(21)304215N; 134(22)318948R; 134(21)303341P

Derwent WPI Acc No: \* C 01-308262; C 01-328500; C 01-308262

Language of Document: English

Patent (Number,Kind,Date): WO 200127347 A1 20010419

METHOD OF DEPOSITING TRANSITION METAL NITRIDE THIN FILMS (English)

Patent Assignee: ASM MICROCHEMISTRY OY (FI); ELERS KAI ERIK (FI); HAUKKA SUDI PAEIVIKKI (FI); SAANILA VILLE ANTERO (FI); KAIPIO SARI JOHANNA (FI); SOININEN PEKKA JUHA (FI)

Author (Inventor): ELERS KAI-ERIK (FI); HAUKKA SUDI PAEIVIKKI (FI); SAANILA VILLE ANTERO (FI); KAIPIO SARI JOHANNA (FI); SOININEN PEKKA JUHA (FI)

Priority (Number,Kind,Date): FI 992234 A 19991015

Applc.(Number,Kind,Date): WO 2000FI1895 A 20001013

Designated States: (National) AE; AG; AL; AM; AT; AU; AZ; BA; BB; BG; BR; BY; BZ; CA; CH; CN; CR; CU; CZ; DE; DE; DK; DK; DM; DZ; EE; EE; ES; FI; FI; GB; GD; GE; GH; GM; HR; HU; ID; IL; IN; IS; JP; KE; KG; KP; KR; KR; LC; LK; LR; LS; LT; LU; LV; MA; MD; MG; MK; MN; MW; MX; MZ; NO; NZ; PL; PT; RO; RU; SD; SE; SG; SI; SK; SK; SL; TJ; TM; TR; TT; TZ; UA; UG; US; UZ; VN; YU; ZA; ZW (Regional) GH; GM; KE; LS; MW; MZ; SD; SL; SZ; TZ; UG; ZW; AM; AZ; BY; KG; KZ; MD; RU; TJ; TM; AT; BE; CH; CY; DE; DK; ES; FI; FR; GB; GR; IE; IT; LU; MC; NL; PT; SE; BF; BJ; CF; CG; CI; CM; GA; GN; GW; ML; MR; NE; SN; TD; TG

Filing Details: WO 100000 With international search report

IPC: \* C23C-016/44; C23C-016/00; C30B-025/02; H05K-003/00

CA Abstract No: \* 134(21)303342Q; 134(21)304215N; 134(22)318948R; 134(21)303342Q

Derwent WPI Acc No: \* C 01-308263; C 01-328500; C 01-308263

Language of Document: English

Patent (Number,Kind,Date): WO 200129280 A1 20010426

DEPOSITION OF TRANSITION METAL CARBIDES (English)

Patent Assignee: ASM INC (US); ELERS KAI ERIK (FI); HAUKKA SUDI PAEIVIKKI (FI); SAANILA VILLE ANTERO (FI); KAIPIO SARI JOHANNA (FI); SOININEN PEKKA JUHA (FI)

Author (Inventor): ELERS KAI-ERIK (FI); HAUKKA SUDI PAEIVIKKI (FI); SAANILA VILLE ANTERO (FI); KAIPIO SARI JOHANNA (FI); SOININEN PEKKA JUHA (FI)

Priority (Number,Kind,Date): FI 992233 A 19991015; FI 992234 A 19991015; FI 992235 A 19991015; FI 20000564 A 20000310; US 159799 P 19991015; US 176948 P 20000118

Applc.(Number,Kind,Date): WO 2000US28537 A 20001016

Designated States: (National) AE; AG; AL; AM; AT; AU; AZ; BA; BB; BG; BR; BY; BZ; CA; CH; CN; CR; CU; CZ; DE; DE; DK; DK; DM; DZ; EE; EE; ES; FI; FI; GB; GD; GE; GH; GM; HR; HU; ID; IL; IN; IS; JP; KE; KG; KP; KR; KR; LC; LK; LR; LS; LT; LU; LV; MA; MD; MG; MK; MN; MW; MX; MZ; NO; NZ; PL; PT; RO; RU; SD; SE; SG; SI; SK; SK; SL; TJ; TM; TR; TT; TZ; UA; UG; US; UZ; VN; YU; ZA; ZW (Regional) GH; GM; KE; LS; MW; MZ; SD; SL; SZ; TZ; UG; ZW; AM; AZ; BY; KG; KZ; MD; RU; TJ; TM; AT; BE; CH; CY; DE; DK; ES; FI; FR; GB; GR; IE; IT; LU; MC; NL; PT; SE; BF; BJ; CF; CG; CI; CM; GA; GN; GW; ML; MR; NE; SN; TD; TG

Filing Details: WO 100000 With international search report

IPC: \* C23C-016/32; H01L-021/00

CA Abstract No: ; 134(22)318948R

Derwent WPI Acc No: ; C 01-328500

Language of Document: English

Patent (Number,Kind,Date): WO 200129891 A1 20010426

CONFORMAL LINING LAYERS FOR DAMASCENE METALLIZATION (English)

Patent Assignee: ASM INC (US)

Author (Inventor): RAAIJMAKERS IVO; HAUKKA SUIV P; GRANNEMAN ERNST H A; SAANILA VILLE ANTERO; SOININEN PEKKA JUHA; ELERS KAI-ERIK

Priority (Number,Kind,Date): US 159799 P 19991015; US 176944 P 20000118

Applc (Number,Kind,Date): WO 2000US23213 A 20000824

Designated States: (National) JP; KR (Regional) AT; BE; CH; CY; DE; DK; ES; FI; FR; GB; GR; IE; IT; LU; MC; NL; PT; SE

Filing Details: WO 120000 With international search report; With amended claims and statement

IPC: \* H01L-021/768; H01L-023/532; C23C-016/00

CA Abstract No: ; 134(21)304079W

Derwent WPI Acc No: ; C 01-328533

Language of Document: English

Patent (Number,Kind,Date): WO 200129893 A1 20010426

METHOD FOR DEPOSITING NANOLAMINATE THIN FILMS ON SENSITIVE SURFACES (English)

Patent Assignee: ASM INC (US); ELERS KAI ERIK (FI); HAUKKA SUIV P (FI); SAANILA VILLE ANTERO (FI); KAIPIO SARI JOHANNA (FI); SOININEN PEKKA JUHA (FI)

Author (Inventor): ELERS KAI-ERIK (FI); HAUKKA SUIV P (FI); SAANILA VILLE ANTERO (FI); KAIPIO SARI JOHANNA (FI); SOININEN PEKKA JUHA (FI)

Priority (Number,Kind,Date): FI 992233 A 19991015; FI 992234 A 19991015; FI 992235 A 19991015; FI 2000564 A 20000310; US 175799 P 19991015; US 176948 P 20000118

Applc (Number,Kind,Date): WO 2000US28654 A 20001016

Designated States: (National) AE; AG; AL; AM; AT; AT; AU; AZ; BA; BB; BG; BR; BY; BZ; CA; CH; CN; CR; CU; CZ; DE; DE; DK; DK; DM; DZ; EE; EE; ES; FI; FI; GB; GD; GE; GH; GM; HR; HU; ID; IL; IN; IS; JP; KE; KG; KP; KR; KR; LC; LK; LR; LS; LT; LU; LV; MA; MD; MG; MK; MN; MW; MX; MZ; NO; NZ; PL; PT; RO; RU; SD; SE; SG; SI; SK; SK; SL; TJ; TM; TR; TT; TZ; UA; UG; US; UZ; VN; YU; ZA; ZW (Regional) GH; GM; KE; LS; MW; MZ; SD; SL; SZ; TZ; UG; ZW; AM; AZ; BY; KG; KZ; MD; RU; TJ; TM; AT; BE; CH; CY; DE; DK; ES; FI; FR; GB; GR; IE; IT; LU; MC; NL; PT; SE; BF; BJ; CF; CG; CI; CM; GA; GN; GW; ML; MR; NE; SN; TD; TG

Filing Details: WO 130000 With international search report; Before expiration of time limit for amending the claims and to be republished in the event of the receipt of the amendments

IPC: \* H01L-021/768; H01L-021/285; C23C-016/00

CA Abstract No: \* 134(21)303341P; 134(21)303342Q; 134(21)304215N; 134(22)318948R; 134(21)304215N

Derwent WPI Acc No: \* C 01-308262; C 01-308263; C 01-328500

Language of Document: English

### World Intellectual Property Organization, PCT (WO) - Legal Status

Number	Type	Date	Code	Text	
WO 200115220	P	19990824	WO AA	PRIORITY CLAIMED	
				US 150486 P 19990824	
WO 200115220	P	19991015	WO AA	PRIORITY CLAIMED	
				US 159799 P 19991015	
WO 200115220	P	20000118	WO AA	PRIORITY CLAIMED	
				US 176944 P 20000118	
WO 200115220	P	20000824	WO AE	APPLICATION DATA	(APPL. DATA)

			WO 2000US23252 A 20000824	
○ WO 200115220	P 20010301	WO AK	DESIGNATED STATES CITED IN A PUBLISHED APPLICATION WITH SEARCH REPORT	(DESIGNATED STATES CITED IN A PUBLISHED APPL. WITH SEARCH REPORT)
			AE AG AL AM AT AU AZ BA BB BG BR BY BZ CA CH CN CR CU CZ CZ DE DE DK DK DM DZ EE EE ES FI FI GB GD GE GH GM HR HU ID IL IN IS JP KE KG KP KR KZ LC LK LR LS LT LU LV MA MD MG MK MN MW MX MZ NO NZ PL PT RO RU SD SE SG SI SK SK SL TJ TM TR TT TZ UA UG US UZ VN YU ZA ZW	
WO 200115220	P 20010301	WO AL	DESIGNATED COUNTRIES FOR REGIONAL PATENTS CITED IN A PUBLISHED APPLICATION WITH SEARCH REPORT	(DESIGNATED COUNTRIES FOR REGIONAL PATENTS CITED IN A PUBLISHED APPL. WITH SEARCH REPORT)
			GH GM KE LS MW MZ SD SL SZ TZ UG ZW AM AZ BY KG KZ MD RU TJ TM AT BE CH CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE BF BJ CF CG CI CM GA GN GW ML MR NE SN TD TG	
○ WO 200115220	P 20010301	WO A1	PUBLICATION OF THE INTERNATIONAL APPLICATION WITH THE INTERNATIONAL SEARCH REPORT	(PUB. OF THE INTERNATIONAL APPL. WITH THE INTERNATIONAL SEARCH REPORT)
WO 200115220	P 20010425	WO 121	EP: THE EPO HAS BEEN INFORMED BY WIPO THAT EP WAS DESIGNATED IN THIS APPLICATION	
WO 200115220	P 20010531	WO DFPE	REQUEST FOR PRELIMINARY EXAMINATION FILED PRIOR TO EXPIRATION OF 19TH MONTH FROM PRIORITY DATE	
WO 200127346	P 19991015	WO AA	PRIORITY (PATENT) FI 992233 A 19991015	
WO 200127346	P 20001012	WO AE	APPLICATION DATA WO 2000FI884 A 20001012	(APPL. DATA)
○ WO 200127346	P 20010419	WO AK	DESIGNATED STATES CITED IN A PUBLISHED APPLICATION WITH SEARCH REPORT	(DESIGNATED STATES CITED IN A PUBLISHED APPL. WITH SEARCH REPORT)
			AE AG AL AM AT AT AU AZ BA BB BG BR BY BZ CA CH CN CR CU CZ CZ DE	

DE DK DK DM DZ EE EE ES FI FI GB GD  
GE GH GM HR HU ID IL IN IS JP KE KG  
KP KR KR KZ LC LK LR LS LT LU LV  
MA MD MG MK MN MW MX MZ NO NZ  
PL PT RO RU SD SE SG SI SK SK SL TJ  
TM TR TT TZ UA UG US UZ VN YU ZA  
ZW

WO	P	20010419	WO	DESIGNATED COUNTRIES FOR REGIONAL PATENTS CITED IN A PUBLISHED APPLICATION WITH SEARCH REPORT	(DESIGNATED COUNTRIES FOR REGIONAL PATENTS CITED IN A PUBLISHED APPL. WITH SEARCH REPORT)
			AL		
WO	P	20010419	WO	GH GM KE LS MW MZ SD SL SZ TZ UG ZW AM AZ BY KG KZ MD RU TJ TM AT BE CH CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE BF BJ CF CG CI CM GA GN GW ML MR NE SN TD TG	
			A1	PUBLICATION OF THE INTERNATIONAL APPLICATION WITH THE INTERNATIONAL SEARCH REPORT	(PUB. OF THE INTERNATIONAL APPL. WITH THE INTERNATIONAL SEARCH REPORT)
WO	P	20010613	WO	EP: THE EPO HAS BEEN INFORMED BY WIPO THAT EP WAS DESIGNATED IN THIS APPLICATION	
		121			
WO	P	20010830	WO	REQUEST FOR PRELIMINARY EXAMINATION FILED PRIOR TO EXPIRATION OF 19TH MONTH FROM PRIORITY DATE	
		DFPE			
WO	P	19991015	WO	PRIORITY (PATENT)	
		AA		FI 992234 A 19991015	
WO	P	20001013	WO	APPLICATION DATA	(APPL. DATA)
		AE		WO 2000FI895 A 20001013	
WO	P	20010419	WO	DESIGNATED STATES CITED IN A PUBLISHED APPLICATION WITH SEARCH REPORT	(DESIGNATED STATES CITED IN A PUBLISHED APPL. WITH SEARCH REPORT)
		AK		AE AG AL AM AT AT AU AZ BA BB BG BR BY BZ CA CH CN CR CU CZ CZ DE DE DK DK DM DZ EE EE ES FI FI GB GD GE GH GM HR HU ID IL IN IS JP KE KG KP KR KR KZ LC LK LR LS LT LU LV MA MD MG MK MN MW MX MZ NO NZ PL PT RO RU SD SE SG SI SK SK SL TJ TM TR TT TZ UA UG US UZ VN YU ZA	

			ZW	
WO 200127347	P	20010419 WO AL	DESIGNATED COUNTRIES FOR REGIONAL PATENTS CITED IN A PUBLISHED APPLICATION WITH SEARCH REPORT	(DESIGNATED COUNTRIES FOR REGIONAL PATENTS CITED IN A PUBLISHED APPL. WITH SEARCH REPORT)
			GH GM KE LS MW MZ SD SL SZ TZ UG ZW AM AZ BY KG KZ MD RU TJ TM AT BE CH CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE BF BJ CF CG CI CM GA GN GW ML MR NE SN TD TG	
WO 200127347	P	20010419 WO A1	PUBLICATION OF THE INTERNATIONAL APPLICATION WITH THE INTERNATIONAL SEARCH REPORT	(PUB. OF THE INTERNATIONAL APPL. WITH THE INTERNATIONAL SEARCH REPORT)
WO 200127347	P	20010613 WO 121	EP: THE EPO HAS BEEN INFORMED BY WIPO THAT EP WAS DESIGNATED IN THIS APPLICATION	
WO 200127347	P	20010816 WO DFPE	REQUEST FOR PRELIMINARY EXAMINATION FILED PRIOR TO EXPIRATION OF 19TH MONTH FROM PRIORITY DATE	
WO 200129280	P	19991015 WO AA	PRIORITY (PATENT)  FI 992233 A 19991015	
WO 200129280	P	19991015 WO AA	PRIORITY (PATENT)  FI 992234 A 19991015	
WO 200129280	P	19991015 WO AA	PRIORITY (PATENT)  FI 992235 A 19991015	
WO 200129280	P	19991015 WO AA	PRIORITY CLAIMED  US 159799 P 19991015	
WO 200129280	P	20000118 WO AA	PRIORITY CLAIMED  US 176948 P 20000118	
WO 200129280	P	20000310 WO AA	PRIORITY (PATENT)  FI 2000564 A 20000310	
WO 200129280	P	20001016 WO AE	APPLICATION DATA  WO 2000US28537 A 20001016	(APPL. DATA)
WO 200129280	P	20010426 WO	DESIGNATED STATES CITED IN A	(DESIGNATED STATES)

200129280	AK	PUBLISHED APPLICATION WITH SEARCH REPORT	CITED IN A PUBLISHED APPL. WITH SEARCH REPORT)
		AE AG AL AM AT AU AZ BA BB BG BR BY BZ CA CH CN CR CU CZ CZ DE DE DK DK DM DZ EE EE ES FI FI GB GD GE GH GM HR HU ID IL IN IS JP KE KG KP KR KR KZ LC LK LR LS LT LU LV MA MD MG MK MN MW MX MZ NO NZ PL PT RO RU SD SE SG SI SK SK SL TJ TM TR TT TZ UA UG US UZ VN YU ZA ZW	
WO P 20010426 WO 200129280	AL	DESIGNATED COUNTRIES FOR REGIONAL PATENTS CITED IN A PUBLISHED APPLICATION WITH SEARCH REPORT	(DESIGNATED COUNTRIES FOR REGIONAL PATENTS CITED IN A PUBLISHED APPL. WITH SEARCH REPORT)
		GH GM KE LS MW MZ SD SL SZ TZ UG ZW AM AZ BY KG KZ MD RU TJ TM AT BE CH CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE BF BJ CF CG CI CM GA GN GW ML MR NE SN TD TG	
WO P 20010426 WO 200129280	A1	PUBLICATION OF THE INTERNATIONAL APPLICATION WITH THE INTERNATIONAL SEARCH REPORT	(PUB. OF THE INTERNATIONAL APPL. WITH THE INTERNATIONAL SEARCH REPORT)
WO P 20010620 WO 200129280	121	EP: THE EPO HAS BEEN INFORMED BY WIPO THAT EP WAS DESIGNATED IN THIS APPLICATION	
WO P 20010816 WO 200129280	DFPE	REQUEST FOR PRELIMINARY EXAMINATION FILED PRIOR TO EXPIRATION OF 19TH MONTH FROM PRIORITY DATE	
WO P 19991015 WO 200129891	AA	PRIORITY CLAIMED  US 159799 P 19991015	
WO P 20000118 WO 200129891	AA	PRIORITY CLAIMED  US 176944 P 20000118	
WO P 20000824 WO 200129891	AE	APPLICATION DATA  WO 2000US23213 A 20000824	(APPL. DATA)
WO P 20010426 WO 200129891	AK	DESIGNATED STATES CITED IN A PUBLISHED APPLICATION WITH SEARCH REPORT	(DESIGNATED STATES CITED IN A PUBLISHED APPL. WITH SEARCH REPORT)

			JP KR	
○ WO 200129891	P	20010426 WO AL	DESIGNATED COUNTRIES FOR REGIONAL PATENTS CITED IN A PUBLISHED APPLICATION WITH SEARCH REPORT	(DESIGNATED COUNTRIES FOR REGIONAL PATENTS CITED IN A PUBLISHED APPL. WITH SEARCH REPORT)
			AT BE CH CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE	
WO 200129891	P	20010426 WO A1	PUBLICATION OF THE INTERNATIONAL APPLICATION WITH THE INTERNATIONAL SEARCH REPORT	(PUB. OF THE INTERNATIONAL APPL. WITH THE INTERNATIONAL SEARCH REPORT)
WO 200129891	P	20010620 WO 121	EP: THE EPO HAS BEEN INFORMED BY WIPO THAT EP WAS DESIGNATED IN THIS APPLICATION	
WO 200129893	P	19991015 WO AA	PRIORITY (PATENT)  FI 992233 A 19991015	
WO 200129893	P	19991015 WO AA	PRIORITY (PATENT)  FI 992234 A 19991015	
○ WO 200129893	P	19991015 WO AA	PRIORITY (PATENT)  FI 992235 A 19991015	
WO 200129893	P	19991015 WO AA	PRIORITY CLAIMED  US 175799 P 19991015	
WO 200129893	P	20000118 WO AA	PRIORITY CLAIMED  US 176948 P 20000118	
WO 200129893	P	20000310 WO AA	PRIORITY (PATENT)  FI 2000564 A 20000310	
WO 200129893	P	20001016 WO AE	APPLICATION DATA  WO 2000US28654 A 20001016	(APPL. DATA)
WO 200129893	P	20010426 WO AK	DESIGNATED STATES CITED IN A PUBLISHED APPLICATION WITH SEARCH REPORT	(DESIGNATED STATES CITED IN A PUBLISHED APPL. WITH SEARCH REPORT)
			AE AG AL AM AT AT AU AZ BA BB BG BR BY BZ CA CH CN CR CU CZ CZ DE DE DK DK DM DZ EE EE ES FI FI GB GD GE GH GM HR HU ID IL IN IS JP KE KG	

KP KR KR KZ LC LK LR LS LT LU LV  
MA MD MG MK MN MW MX MZ NO NZ  
PL PT RO RU SD SE SG SI SK SK SL TJ  
TM TR TT TZ UA UG US UZ VN YU ZA  
ZW

WO	P	20010426	WO	DESIGNATED COUNTRIES FOR REGIONAL PATENTS CITED IN A PUBLISHED APPLICATION WITH SEARCH REPORT	(DESIGNATED COUNTRIES FOR REGIONAL PATENTS CITED IN A PUBLISHED APPL. WITH SEARCH REPORT)
200129893			AL		
WO	P	20010426	WO	PUBLICATION OF THE INTERNATIONAL APPLICATION WITH THE INTERNATIONAL SEARCH REPORT	(PUB. OF THE INTERNATIONAL APPL. WITH THE INTERNATIONAL SEARCH REPORT)
200129893			A1		
WO	P	20010620	WO	EP: THE EPO HAS BEEN INFORMED BY WIPO THAT EP WAS DESIGNATED IN THIS APPLICATION	
200129893			121		
WO	P	20010802	WO	REQUEST FOR PRELIMINARY EXAMINATION FILED PRIOR TO EXPIRATION OF 19TH MONTH FROM PRIORITY DATE	
200129893			DFPE		

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